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(54) Title: ADDITIVES FOR CONTROLLING OR MODIFYING RHEOLOGICAL PROPERTIES

(57) Abstract

An amine salt of a partially esterified highly carboxylated polymer is used in a substantially non-polar solvent as a viscosifier for liquid or semi-liquid compositions such as drilling muds, coating compositions etc. A preferred polymer is a co-polymer of maleic anhydride and isobutylene and the ester is preferably formed from a long chain alcohol, the amine salt preferably being formed from a long chain amine.

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Title:- "Additives for controlling or modifying rheological properties"

Description of Invention

This invention relates to materials for use as additives for controlling or modifying rheological properties of systems such as drilling muds, paints and many other liquid or semi-liquid compositions.

One commonly used type of such additive comprises organoclays, that is
5 to say clays of the Bentonite type which have been reacted with a quaternary ammonium compound, especially such a compound containing long chain carbon radicals. Such organoclays are useful in practice but suffer from a number of disadvantages, including cost and availability of raw materials, the often limited applicability of specific organoclays for specific systems, and
10 undesirable variation of the thixotropic properties of the system in use.

For example, the parameters known as "yield point" and "gel strength" are particularly significant respectively in relation to the shear thinning property and the ability of the liquid to support the solid constituents of the system in suspension. It is well known that in organoclay-containing drilling
15 mud systems the values of the yield point and gel strength change in use from initial values which apply to the system as initially prepared to aged values which apply to the system after a period of use. The initial values need to be sufficiently high to maintain solids in suspension, but since ageing normally increases these values it should be not so high initially as to make the system
20 excessively viscous when aged.

Attempts to provide new organoclays using different quaternary ammonium compounds have met with some success, but at the cost of requiring expensive starting materials which are not always readily available in commercial quantities.

25 Various alternatives to organoclays have also been proposed, most notably organic polymers of different kinds, but such materials also tend to be expensive to produce and are more likely to be unstable at higher temperatures so that their thixotropic properties may be impaired or destroyed when the system is in use.

The present invention relates to a particular species of organic polymer which is advantageously capable of use especially in oil-based drilling muds and other substantially non-polar systems.

According to the invention a substantially non-polar liquid or semi-liquid composition incorporates, as an additive to increase its viscosity, an amine salt of a partially esterified highly carboxylated polymer.

The invention also resides in an additive for addition to a substantially non-polar liquid or semi-liquid composition, the additive comprising a gel formed from a substantially non-polar solvent containing an amine salt of a partially esterified highly carboxylated polymer.

Such amine salts have an ionic character in substantially non-polar solvents. It is known that ion-containing polymers interact by a primarily physical mechanism which causes cross-linking of the polymer chains as a result of the formation of clusters of ion-pairs into domains. This may be contrasted with other polymeric materials proposed for use as viscosifiers, which can be divided into one group in which the polymer chains are cross-linked by covalent chemical linkages and another group in which high molecular weight polymers interact weakly.

Other ion-containing polymers previously proposed for use as viscosifiers, for example sulphonated polymers, have various disadvantages which are avoided by the present invention, including difficulties in availability of starting materials, in manufacturing processes, toxicity and so on.

The amine salts used in accordance with the invention are preferably derived from a highly carboxylated polymer having an average molecular weight in excess of 1000, and more preferably in excess of 10,000. The polymer is preferably such that carboxyl groups or precursors of carboxyl groups are present on at least 25%, more preferably at least 50%, of the carbon atoms in the polymeric chain. The polymer may be derived from a polybasic acid monomer, particularly a dibasic acid, alone or in combination with an alkylene monomer, and preferably in the form of its anhydride. A particularly preferred polymer is a co-polymer of maleic anhydride and isobutylene, although other similar co-polymers may be employed.

The partial ester is preferably formed by means of a long chain alcohol, or a mixture of long chain alcohols, i.e. with carbon chains of at least 8, and preferably 13 to 25 carbon atoms.

The amine used for the preparation of the amine salt of the partially esterified polymer may be a primary or secondary amine, or a substituted amine, preferably a long chain amine, i.e. with carbon chains of at least 8, and preferably 13 to 25 carbon atoms, although in some cases a short chain amine may be employed. Particularly preferred amines include amines derived from tallow, including tallow amine and hydrogenated-tallow amines, such as methyl di-hydrogenated-tallow amine and the like.

Examples of amine salts used in accordance with the invention are set out in table 1, where the polymer, alcohol and amine used in each example are identified.

In each example, a quantity of the polymer was introduced into a reaction vessel with an appropriate quantity of the selected alcohol and zinc acetate as a catalyst. The reactants were dissolved in toluene and the reaction was conducted under reflux in a Dean & Stark apparatus, the water formed in the reaction being distilled from the reactants. The reaction proceeds in two stages; firstly a rapid reaction involving the opening of the anhydride rings to form the half ester and secondly a slower reaction involving esterification of some of the carboxyl groups of the half ester. When substantially all of the alcohol had been combined with the polymer, there was present in the reaction vessel a viscous solution of the partial ester. As soon as possible after completion of the reaction, the viscous solution was taken up in the minimum amount of isopropanol solvent and was then treated with a solution of the stated amine in isopropanol to form an amine salt with the unreacted carboxyl groups of the partial ester. The amine was added in a step-wise manner whilst the contents of the reaction vessel were stirred. Addition of the amine was continued until no further reaction was evident. There resulted a white, gelatinous mass which was separated from the solvent and washed with cold isopropanol solvent, filtered and dried in an oven at 40°C. The resulting solid was milled in a centrifugal mill to give an amine salt in the form of a white powder.

The amine salt was dispersed by stirring in a variety of relatively non-polar solvents, including white spirit, xylene, a commercially available diesel oil drilling mud system and a commercially available low toxicity oil drilling mud system. The viscosity of each dispersion was measured at intervals after stirring in the case of the white spirit and xylene systems, and in the case of the drilling mud systems before and after ageing at 250°F for 16 hours. Some illustrative results are set out in Tables 2,3 and 4.

The viscosity of the gels prepared by dispersing the amine salts in white spirit and in xylene was measured at 10, 20, 50 and 100 rpm on a Brookfield viscometer. The same measurements were also carried out for comparison purposes on a gel formed by dispersing in white spirit two commercially available organoclays, namely the reaction product of bentonite clays and a long chain quaternary ammonium compound. The results of these measurements are represented in Table 2. It will be noted that the behaviour of the two gels of salts in white spirit as represented in Table 2 is similar to the behaviour of the two gels formed with conventional organoclays, as will also be evident from Figure 1 which illustrates graphically the results of Examples 5, 7 and A.

The results given in Table 2 show that the tallow amine salts of maleic anhydride-isobutylene co-polymer partial esters exhibit shear-thinning rheology in non-polar solvents such as white spirit. However, tests in more polar systems such as xylene gave clear viscous solutions with near-Newtonian rheology, showing the specific adaption of such salts for use in systems having minimum polar nature.

In Table 3, a further comparison of salts in accordance with the present invention with a known organoclay is made. The results set out in Table 3 were obtained with dispersions of the salts and of the organoclay in a commercially available diesel-oil invert mud system with a continuous oil phase with approximately 20% water content in dispersion. Table 4 shows similar results obtained with dispersions of the amine salts and of the known organoclays in a further invert drilling mud system comprising a commercially available low-toxicity oil which is a mixture consisting mainly of alkanes and cyclo-alkanes and substantially free of aromatic hydrocarbons.

In the case of these drilling muds a clear distinction was observed in the performance of the gellants in the rather more polar diesel oil and the less polar clean oil systems. In the diesel oil system (Table 3) an initial rheology generally developed, but the gel strength was lost after ageing at 250°F. This has been attributed to the complete dissolution of the polymer in the diesel oil.

In the clean oil system (Table 4), which is based on a highly non-polar mineral oil the observed initial rheology was found to increase on ageing at 250°F to give a high yield point and gel strength at gellant concentrations below 5 ppb. Accordingly, the amine salts were found to be useful in such a drilling mud for achieving suitable viscosity and imparting anti-settling properties to the mud.

5 The amine salts are expected also to be useful as viscosifiers in other liquid or some liquid compositions including coating compositions, lacquer removers, lubricating greases, packer fluids used in wells and in binders for foundry sands. Tests have been carried out with satisfactory results for example in a chlorinated rubber paint. Using the salt of Example 6 in such a paint provided improved sag resistance as compared with a control sample.

10 The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method of process for attaining the disclosed result, or a class or group of substances or compositions, as appropriate, may separately or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

TABLE I

AMINE SALTS OF PARTIALLY ESTERIFIED POLYMERIC ACIDS

Example	Acid	Alcohol	Amine	% free acid ⁽¹⁾
1	Isobam 04 ⁽²⁾	2-ethylhexan-1-ol	Armeen T ⁽⁵⁾	80
2	Isobam 04 ⁽²⁾	2-ethylhexan-1-ol	Armeen M2HT ⁽⁶⁾	80
3	Isobam 10 ⁽³⁾	Dobanol 25 ⁽⁴⁾	Armeen TD ⁽⁷⁾	84
4	Isobam 10 ⁽³⁾	Dobanol 25 ⁽⁴⁾	Armeen TD ⁽⁷⁾	77
5	Isobam 10 ⁽³⁾	Dobanol 25 ⁽⁴⁾	Armeen 2HT ⁽⁸⁾	75
6	Isobam 10 ⁽³⁾	2-ethylhexan-1-ol	Armeen TD ⁽⁷⁾	85

- (1) in partial ester, as percentage maximum carboxyl groups available in half-ester in the first stage of the reaction involving the opening of the anhydride rings, and based on moles of H₂O produced during esterification.
- (2) a commercial grade of maleic anhydride/isobutylene co-polymer having a molecular weight of $5.5 - 6.0 \times 10^4$ from Revertex Limited.
- (3) a commercial grade of maleic anhydride/isobutylene co-polymer having a molecular weight of $16 - 17 \times 10^4$ from Revertex Limited.
- (4) a commercial grade of straight chain C₁₅ - C₁₃ alcohol from Shell Chemicals.
- (5) a commercial grade of tallow amine from Akzo Limited.
- (6) a commercial grade of methyl di-hydrogenated-tallow amine from Akzo Limited
- (7) a commercial grade of purified tallow amine from Akzo Limited
- (8) a commercial grade of di-hydrogenated-tallow amine from Akzo Limited.

TABLE 2

AMINE SALTS IN NON-POLAR SOLVENTS

Ex. No.	Gellant	Solvent	%w/w	Time After Mixing Hours	Brookfield viscosity cP at 25°C			
					10 rpm	20 rpm	50 rpm	100 rpm
7	Salt of Ex.1	White spirit	11.1	2	4640	3000	1190	794
				16	4400	3600	1160	816
8	Salt of Ex.1	Xylene	7.0	2	600	590	574	620
9	Salt of Ex.2	White spirit	5.9	16	1860	1175	636	439
				96	5360	4610	2920	1900
A	Organoclay A ⁽¹⁾	White spirit	2.0 ⁽³⁾	1	1780	790	352	194
B	Organoclay B ⁽²⁾	Xylene	2.0 ⁽³⁾	1	1984	1102	372	202

(1) a conventional Montmorillonite-based wet process organoclay of high purity.

(2) a conventional Hectorite-based wet process organoclay.

(3) Standard 2.0% gel with polar additive in a Waring blender.

TABLE 3
AMINE SALTS IN DIESEL OIL SYSTEM ⁽¹⁾

Ex. No.	Gellant	ppb gellant	Fann Rheology at 115°F					
			Initial			Aged		
			PV	YP	Gels ⁽²⁾	PV	YP	Gels ⁽²⁾
10	Salt of Ex.1	10	74	40	34/50	55	31	2/3
11	Salt of Ex.2	5	22	7	3/13	32	8	4/5
12	Salt of Ex.2	10	33	13	6/12	36	2	2/2
13	Salt of Ex. 2	20	100	70	93/126	--	--	--
14	Salt of Ex. 4	4	23	5	2/3	23	2	2/2
C	Organoclay C	8	29	23	14/17	33	23	15/22

(1) Mud weight = 12ppg; oil/water ratio=85/25; water activity AW=0.75.

(2) Gel strength lb/100ft.² after 10 Sec/10 min

(3) a conventional Montmorillonite-based dry process organoclay specifically for use in drilling mud systems.

TABLE 4
AMINE SALTS IN LOW TOXICITY OIL SYSTEM⁽¹⁾

Ex. No.	Gellant	ppb gellant	Fann Rheology at 115°F					
			Initial			Aged		
			PV	YP	Gels ⁽²⁾	PV	YP	Gels ⁽²⁾
15	Salt of Ex. 1	10 ⁽³⁾	32	4	4/11	73	166	55/85
16	Salt of Ex.3	5	14	1	2/2	60	73	19/57
17	Salt of Ex.3	4	12	0	2/2	41	27	5/11
18	Salt of Ex.4	5	41	24	3/14	74	103	25/57
19	Salt of Ex.4	4	28	4	2/4	66	80	22/47
20	Salt of Ex.5	4	35	11	8/14	47	36	10/28
D	Organoclay D ⁽⁴⁾	10	36	14	10/18	51	51	31/62
E	Organoclay E ⁽⁵⁾	10	22	1	2/2	40	18	10/23

(1) Mud weight 12 ppg; oil water ratio=80/20; water activity AW=0.75.

(2) Gel strength lb/100 ft² after 10 Sec/10 min.

(3) No fluid loss additive.

(4) a conventional Hectorite-based wet process organoclay.

(5) a conventional Montmorillonite-based dry process clay specifically for use in drilling muds.

CLAIMS:-

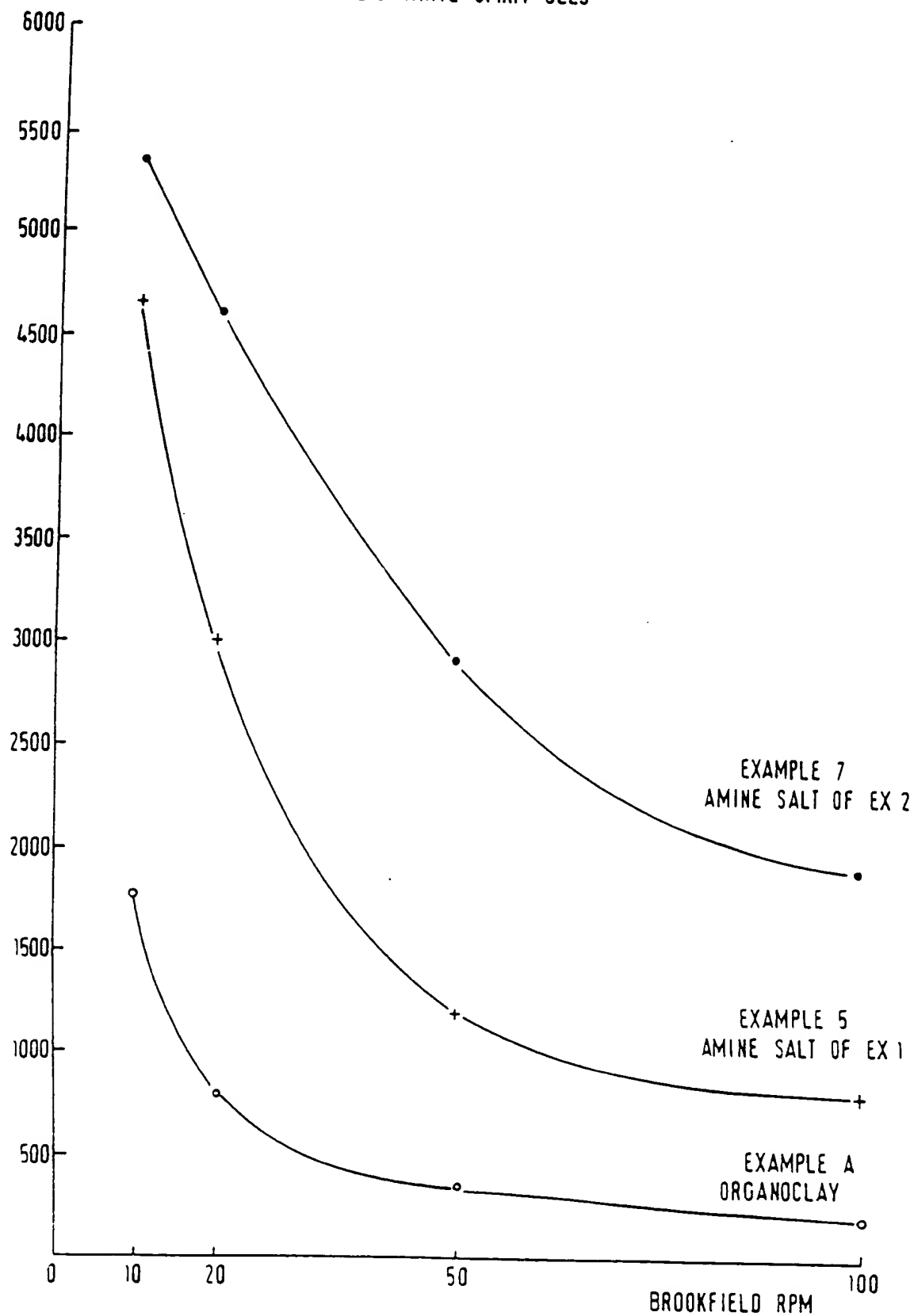
1. A substantially non-polar liquid or semi-liquid composition incorporating, as an additive to increase its viscosity, and amine salt of a partially esterified highly carboxylated polymer.
2. A composition according to Claim 1 wherein the amine salt is derived
5 from a highly carboxylated polymer having an average molecular weight in excess of 1000.
3. A composition according to Claim 2 wherein the average molecular weight of the polymer is in excess of 10,000.
4. A composition according to any one of the preceding claims wherein the
10 amine salt is derived from a polymer in which carboxyl groups or precursors of carboxyl groups are present on at least 25% of the carbon atoms in the polymeric chain.
5. A composition according to Claim 4 wherein carboxylic groups or
15 precursors of carboxyl groups are present on at least 50% of the carbon atoms of the polymeric chain.
6. A composition according to any one of the preceding claims wherein the polymer is derivative of a polybasic acid monomer.
7. A composition according to Claim 6 wherein the acid monomer is a dibasic acid.
8. A composition according to any one of the preceding claims wherein the
20 polymer is a co-polymer of a carboxylic acid or anhydride and an alkylene.
9. A composition according to Claim 8 wherein the polymer is a co-polymer of maleic anhydride and isobutylene.
10. A composition according to any one of the preceding claims wherein the
25 partial ester of a polymer is formed from an alcohol or a mixture of alcohols having a carbon chain length of at least 3.

21. An amine salt of a partially esterified highly carboxylated polymer substantially as hereinbefore described with reference to and as described in any one of Examples 1 to 6 herein.
22. An additive as claimed in Claim 19 and substantially as hereinbefore described in Examples 7 and 9 herein.
23. A composition according to Claim 1 and substantially as hereinbefore described in any one of Examples 15 to 20 herein.

11. A composition according to Claim 10 wherein the alcohol has a chain length between 13 and 25 carbon atoms.
12. A composition according to any one of the preceding claims wherein the amine from which the amine salt is derived is a primary or secondary amine, or a substituted amine.
13. A composition according to Claim 12 wherein the amine has at least one carbon chain of at least 8 atoms.
14. A composition according to Claim 12 wherein the amine has at least one carbon chain of a length of between 13 and 25 carbon atoms.
15. A composition according to any one of the preceding claims wherein the amine from which the amine salt is derived is a tallow amine.
16. A composition according to Claim 15 wherein said tallow amine is an hydrogenated tallow amine.
17. A composition according to Claim 16 wherein said tallow amine is di-hydrogenated-tallow amine.
18. A composition according to Claim 16 wherein said amine is methyl di-hydrogenated tallow amine.
19. An additive for addition to a substantially non-polar liquid or semi-liquid composition for the purpose of increasing the viscosity of said composition, the additive comprising a gel formed from a substantially non-polar solvent containing a dispersion of an amine salt of a partially esterified highly carboxylated polymer.
20. A method of increasing the viscosity of a substantially non-polar liquid or semi-liquid composition comprising the step of incorporating in said composition a dispersion of an amine salt of a partially esterified highly carboxylated polymer.

BROOKFIELD
VISCOSITY CP

FIGURE I WHITE SPIRIT GELS



ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/GB 86/00662 (SA 14992)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 19/02/87

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4505833	19/03/85	None	
US-A- 2217926		None	

INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 86/00662

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 09 K 7/00; C 09 K 3/00; C 09 D 7/00 D											
II. FIELDS SEARCHED <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System ¹</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; vertical-align: top;">IPC⁴</td> <td style="border: none; vertical-align: top;">C 09 K; C 09 D</td> </tr> </table> <div style="text-align: center; margin-top: 10px;"> <small>Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</small> </div>			Classification System ¹	Classification Symbols	IPC ⁴	C 09 K; C 09 D					
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IPC ⁴	C 09 K; C 09 D										
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border: none;"> <tr> <th style="width: 10%; border: none;">Category ¹⁰</th> <th style="width: 70%; border: none;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border: none;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: none; vertical-align: top; padding: 5px;">A</td> <td style="border: none; vertical-align: top; padding: 5px;">US, A, 4505833 (S.A. LIPOVSKI) 19 March 1985 see column 1, lines 54-68; column 2, lines 1-28, 56-63; column 4, lines 6-41; column 5, lines 2-25; claims 1-12</td> <td style="border: none; vertical-align: top; padding: 5px;">1, 6, 7, 12, 19, 20</td> </tr> <tr> <td style="border: none; vertical-align: top; padding: 5px;">A</td> <td style="border: none; vertical-align: top; padding: 5px;">US, A, 2217926 (P.V. CAMPEN) 15 October 1940 see page 1, lines 25-44; claims 1-10 -----</td> <td style="border: none; vertical-align: top; padding: 5px;">1</td> </tr> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US, A, 4505833 (S.A. LIPOVSKI) 19 March 1985 see column 1, lines 54-68; column 2, lines 1-28, 56-63; column 4, lines 6-41; column 5, lines 2-25; claims 1-12	1, 6, 7, 12, 19, 20	A	US, A, 2217926 (P.V. CAMPEN) 15 October 1940 see page 1, lines 25-44; claims 1-10 -----	1
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A	US, A, 2217926 (P.V. CAMPEN) 15 October 1940 see page 1, lines 25-44; claims 1-10 -----	1									
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><small>* Special categories of cited documents: ¹⁴</small></p> <p><small>"A" document defining the general state of the art which is not considered to be of particular relevance</small></p> <p><small>"E" earlier document but published on or after the international filing date</small></p> <p><small>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</small></p> <p><small>"O" document referring to an oral disclosure, use, exhibition or other means</small></p> <p><small>"P" document published prior to the international filing date but later than the priority date claimed</small></p> </div> <div style="width: 45%;"> <p><small>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</small></p> <p><small>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</small></p> <p><small>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</small></p> <p><small>"Z" document member of the same patent family</small></p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <small>Date of the Actual Completion of the International Search</small> <div style="text-align: center; margin-top: 5px;">11th February 1987</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> <small>Date of Mailing of this International Search Report</small> <div style="text-align: center; margin-top: 5px;">25 FEB. 1987</div> </td> </tr> <tr> <td style="border: none; vertical-align: top;"> <small>International Searching Authority</small> <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none; vertical-align: top;"> <small>Signature of Authorized Officer</small> <div style="text-align: center; margin-top: 10px;">M. VAN MUL </div> </td> </tr> </table>			<small>Date of the Actual Completion of the International Search</small> <div style="text-align: center; margin-top: 5px;">11th February 1987</div>	<small>Date of Mailing of this International Search Report</small> <div style="text-align: center; margin-top: 5px;">25 FEB. 1987</div>	<small>International Searching Authority</small> <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div>	<small>Signature of Authorized Officer</small> <div style="text-align: center; margin-top: 10px;">M. VAN MUL </div>					
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